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Gas-surface scattering : A review of quantum statistical approach

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Abstract : The quantum theory of scattering of gas atoms from solid surfaces is reviewed with special reference to ^{4}He gas scattering from Graphite and Argon surfaces It has been emphasised that the sticking coefficients and the bound state lifetimes evaluated from T-matrix formalism are more exact and take into account the problems of overcounting of scattering events encountered in usual first order distorted wave Born approximation (FODWBA).

Keywords : Scattering, T-matrix, FODWBA

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1. Introduction

The gas-surface scattering refers to processes initiated at a surface and involving atoms of both the gas and the solid. It is only the scattering of gas atoms which may be studied by experiments.

Particles adsorbed by weak van-der Waals forces are said to be physically adsorbed or physisorbed *e.g.* rare gases on metals, alkali halides and on graphite. One of the most important processes occurring at a gas-solid interface is the capture and subsequent sticking of incident atoms or molecules. If we want to know how fast and by what mechanism a gas particle adsorbs on or desorbs from a solid, we have to study its kinetics.

There exists in general two types of theories describing the interaction of particles with a surface those based on classical mechanics for the incoming particle, but nevertheless allowing quantum effects for the substrate and those based on quantum mechanics. Rather peculiarly, the quantum description [1–4] predates the classical one [5,6]. As the quantum theory becomes better developed and is able to interpret more and

more of the forthcoming experimental data, it has become clear that more information on gas-surface scattering is obtainable from experimental data needing a quantum mechanical interpretation than from data for which classical interpretation is inadequate.

In this review we look into some theoretical aspects of gas-surface interaction within the quantum regime from the simple model of gas-solid interaction and discuss some of the interesting results obtained.

The sticking coefficient is one of the most important but unfortunately a very controversial parameter in the study of desorption and evaporation as well as atomic beam scattering. This is particularly true for physisorption where few experimental data are explained by too-many and often inconclusive theories. Classical theories obtain a sticking coefficient of unity as the temperature of the solid approaches zero whereas quantum mechanical theories yield the zero sticking coefficient at zero substrate temperature Thermal accommodation and adsorption coefficients of gases have been reviewed comprehensively by Saxena and Joshi [7].

2. Quantum theory of gas-surface scattering

Almost all the quantum theories dealt in references [1–4] are now understood to be unsatisfactory as they are based on FODWBA. Gas-surface scattering is too strong to be correctly described by FODWBA. In FODWBA, the probability of scattering into one or more final states sometimes exceeds unity (He on graphite). The first-order theories do not generally conserve the number of scattering particles and is non-unitary. There are two closely related methods *viz.* close-coupling formulation (CCF) [8,9] and Cabrera, Celli, Goodmann and Manson approximation (CCGMA) [10] which are unitary as they are almost exact and obtained by deriving the exact wave-function results from T-matrix formalism.

The most suitable formulation for our purposes is the two potential T-matrix scattering theory due to Gellmann and Goldberger [11].

2.1. *T-matrix formalism*:

The Hamiltonian H of the gas atom plus solid including internal states is

$$H = H_0 + U \tag{1}$$

where H_0 is the Hamiltonian for the free gas atom plus the solid and U is the gas-solid interaction part given by

$$U = U_0 + U_1 \tag{2}$$

where U_0 is the large potential depending only on z and is treated exactly and U_1 is the small potential treated approximately. The transition rate from some initial state i (of total energy E_i) to some final state f (of total energy E_f) is

$$P_{fi} = \left(\frac{2\pi}{\hbar}\right)\left|T_{fi}\right|^2 \delta(E_f - E_i) \tag{3}$$

A standard result of the T-matrix is

$$T_{fi} = \langle \Psi_f | U_0 + U_1 | \Psi_i^+ \rangle = \langle \Psi_f | U_0 | \chi_i^+ \rangle + \langle \chi_i^- | U_1 | \Psi_i^+ \rangle \tag{4}$$

where Ψ_a is the solution of Schrödinger equation with Hamiltonian H_0, $\chi_a^{\pm}$ are the incoming wave (–) and outgoing wave (+) solutions with Hamiltonian $H_0 + U_0$ and $\chi_a^{\pm}$ are the solutions of incoming wave (–) and outgoing wave (+) with complete Hamiltonian $H_0 + U_0 + U_1$. The explicit forms of Ψ_a and $\chi_a^{\pm}$ are

$$\Psi_a = (L_x L_y L_z)^{-\frac{1}{2}} |\{n_{ma}\}\rangle e^{i\mathbf{k}_a \cdot \mathbf{R}} e^{iK_{az}z}$$

$$\chi_a^{\pm} = (L_x L_y)^{-\frac{1}{2}} |\{n_{ma}\}\rangle e^{i\mathbf{k}_a \cdot \mathbf{R}} \chi^{\pm}(k_{az}; z) \tag{5}$$

where $|\{n_{ma}\}\rangle$ is the solid vibrational eigenfunction of H_0 labelled by the phonon occupation numbers n_{ma} of the normal modes m, $(L_x L_y)^{-\frac{1}{2}} e^{i\mathbf{k}_a \cdot \mathbf{R}}$ is the plane wave gas atom eigenfunction of H_0 (or of $H_0 + U_0$ because U_0 depends only on z), for motion tangential to the surface, $L_z^{-\frac{1}{2}} e^{iK_{az}z}$ is the plane wave gas atom eigenfunction of H_0 for motion normal to the surface.

Now the T-matrix equation may be written in terms of reduced t-matrix as [12]

$$T_{fi} e^{i\xi_i} = t_{fi} + (i/2\pi\rho_s)\delta(fs)$$

$$|T_{fi}|^2 = |t_{fi} + (1/2\pi\rho_s)\delta(fs)|^2$$

$$t_{fi} = \langle \chi_f^- | U_1 | \Psi_i^+ \rangle e^{-i\xi_i}$$

$$\chi_i^+ = \chi_s^- e^{i\xi_i} \tag{6}$$

for the phase angle $\xi_i = \xi_s$.

The reduced t-matrix may be written as

$$t_{fi} = \langle f|U|s\rangle + \sum_c (E_i - E_c + i\varepsilon)^{-1} \langle f|U|c\rangle t_{ci} + \sum_b (E_i - E_b + i\varepsilon)^{-1} \langle f|U|b\rangle t_{bi} \tag{7}$$

where s, b and c are scattered, bound and continuum states respectively. The summation over continuum states may be written as the product of summations over phonon states, gas atom tangential wave vector states and gas atom normal wave vector states as the following

$$\sum \rightarrow \sum \sum_{k_t} \sum_{k_z} \tag{8}$$

Further, $\sum_{k_{cz}} \rightarrow \int \rho_c dE_{cz}$ where ρ_c is the density of states.

$$\sum_b (E_i - E_b + i\varepsilon)^{-1} \rightarrow (E_i - E_b)^{-1}$$

The integral continuum states (c) does cause a problem and $(E_i - E_c + i\varepsilon)^{-1}$ must be interpreted as

$$\int \frac{f(E_{cz})dE_{cz}}{E_i - E_c + i\varepsilon} = \int \frac{(E_i - E_c - i\varepsilon)f(E_{cz})dE_{cz}}{(E_i - E_c)^2 + \varepsilon^2}$$
$$\rightarrow P\int \frac{f(E_{cz})dE_{cz}}{E_i - E_c} - i\pi \int f(E_c z)\delta(E_i - E_c)dE_{cz} \tag{9}$$

The final result in the exact analysis of the gas atoms is

$$t_{fi} = \langle f|U|s\rangle + \sum_{\{n_{mb}\}} \sum_{k_b} \sum_{k_{bz}} (E_i - E_b)^{-1} \langle f|U|b\rangle t_{bi}$$
$$+ \sum_{\{n_{mc}\}} \sum_{k_c} P\int dE_{cz} (E_i - E_c)^{-1} \rho_c \langle f|U|c\rangle t_{ci} \tag{10}$$
$$- i\pi \left\{ \sum_{\{n_{mc}\}} \sum_{k_c} \rho_c \langle f|U|c\rangle t_{ci} \right\}_{E_c = E_n}$$

$\{\cdots\}$ indicates that only states c satisfying $E_c = E_i$ are considered.

3. Approximations

1. FODWBA : Retains only the first term on the right-hand-side of equation (10)

   $$t_{fi} = \langle f|U|s\rangle \text{ FODWBA}$$

   If $\langle f|U|s\rangle$ are small unitary would hold, at least approximately.

2. CCGMA : The principal part in equation (10) poses major difficulty in solving the reduced t-matrix. In CCGMA we set $P = 0$ *i.e.* all intermediate continuum states c which do not conserve energy exactly are neglected and all intermediate bound states b are included.

Generally gas-surface scattering is strong and $\langle f|U|s\rangle$ are large and therefore FODWBA is generally invalid.

4. Present work

The inadequacy of FODWBA to explain the total inelastic component of the gas-solid interaction has been discussed in detail in our earlier work [13] with specific examples of He scattering from graphite and Ar surfaces. The detailed calculations done in this work for sticking coefficient and bound state lifetimes will not be presented here. Only the results obtained in this case which highlight the importance of exact T-matrix calculation for light particles scattered with very low energy will be discussed.

For very low energy and light particles, the mechanism is intimately related to the quantum nature of incoming particles. In all experiments in which He or H_2 are scattered from single crystal surfaces both inelastic scattering and selective absorption processes are present which can have very important effects on elastic scattering. The inelastic scattering is generally enhanced by selective adsorption resonances so much so that the FODWBA breaks down. The breakdown of FODWBA is caused by overcounting of the scattering events that is inherent in the FODWBA. This overcounting has been removed by renormalisation of the momentum dependent sticking.

5. Discussions

With the above theoretical background, we study the inelastic components in presence of selective bound state (BS) resonances. We hope that a detailed qualitative discussion can be made for sticking of light particles on the cold solid surfaces. It has been shown earlier [14] that the inelastic scattering is greatly enhanced by selective adsorption resonances so much so that the DWBA breaks down. This breakdown caused by the overcounting of the scattering events can be removed by renormalisation of the momentum dependent sticking coefficient within the time of interaction with the surface [15]. We have demonstrated in reference [13] that the problem of overcounting can be tackled by exact T-matrix calculations without recourse to renormalisation considering the inelastic scattering in presence of bound state resonances. We agree that the overcounter of the scattering events can be removed without going beyond one phonon emission/absorption process. We have shown in our earlier work [13] that the overcounting of the scattering events can be largely reduced by considering the inelastic events in presence of bound state resonances even under DWBA. The results of calculations on sticking coefficients with substrate temperature using T-matrix formalism (given in reference 13) are shown in Figures 1–3. In this work we have used the gas temperature T_g = 65 K for He-graphite system and T_g = 55 K for He-Ar system. The essential feature of this work is based on the scattering of He^4 from cold graphite and argon surfaces with extended particle phonon interactions. This leads to the inelastic scattering in presence of resonant surface bound states. The inelastic scattering is however sufficiently weak where only one or two phonons are created or destroyed, it is never negligible. The scattering process can resonably be described in terms of how the occupation of the lattice has changed.

It is observed from Figures 1 and 2 that the sticking component is enhanced with temperature of the substrate thereby indicating the enhancement of the inelastic scattering in terms of the changes in phonon modes because the inelastic scattering probability reflects the discrete nature of the phonon exitation of each mode. It is interesting to note that the inelastic scattering and hence the sticking coefficient is never greater than unity as is found in the case of DWBA. Thus within the one-phonon approximation, if the higher-order terms are taken into account in the perturbation expansion, as we do in the exact T-matrix

calculation, the overcounting of the scattering events inherent in the Born approximation can be removed in presence of surface bound state.

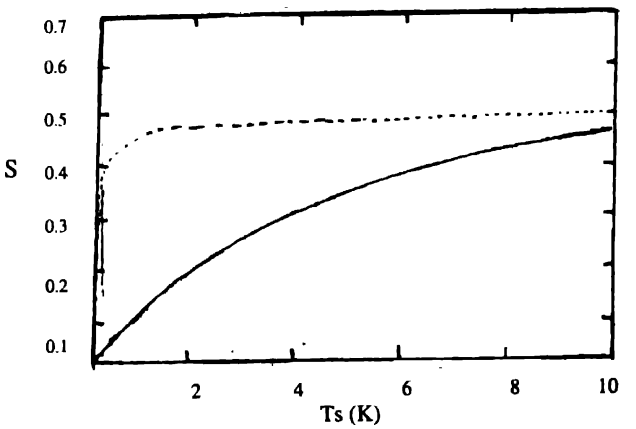

Figure 1. Variation of sticking coefficient with solid temperature for He–Ar system. (Dotted line . results from Reference 15; Solid line : result from *T*-matrix calculations).

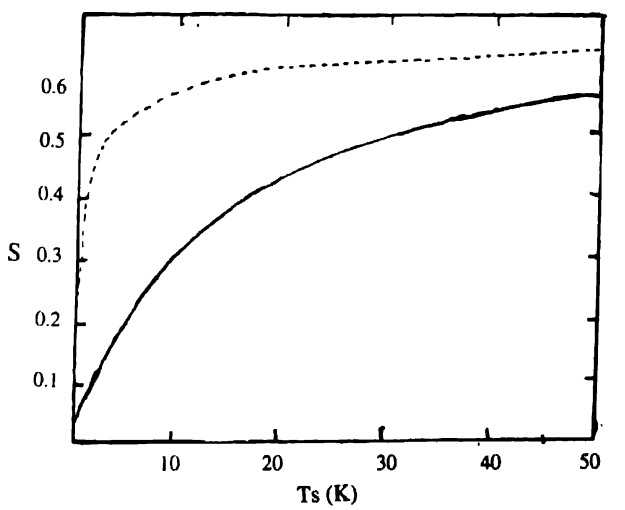

Figure 2. Variation of sticking coefficient with solid temperature for He–graphite system (Dotted line results from Reference 15; Solid line . result from *T*-matrix calculations).

The bound state life times shown in Figure 3 for He–Ar and He–graphite systems indicate that the decay of the bound states are faster at higher temperatures leading to faster desorption. The sticking in these systems are more probable upto a temperature of 10 K as found in experiments.

We thus conclude that the T-matrix formalism which takes into account the higher-order contribution to sticking coefficient of a phonon-mediated process predicts a non-zero

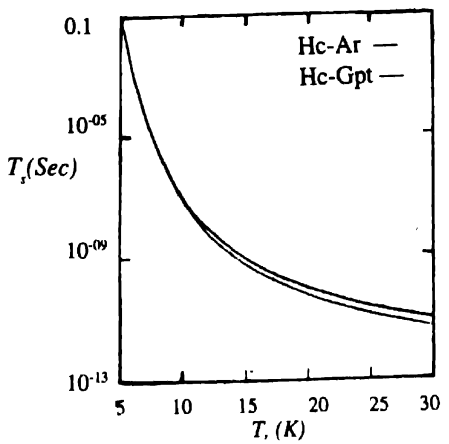

Figure 3. Bound state life times τ_s *vs* substrate temperature

capture even at higher temperatures to make accurate measurements of sticking coefficients difficult, the calculations presented in reference [13] suggest that at higher temperature capture into the physisorption bound state is possible and can be monitored through careful measurements of specular beam. The results, however, depend on the nature of the potential, its well depth and the interaction strength.

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